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A RAPID SEQUENTIAL TRACER GAS ANALYZER SUITABLE FOR USE IN THE UNDERGROUND ENVIRONMENT

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A RAPID SEQUENTIAL TRACER GAS ANALYZER SUITABLE FOR USE IN THE UNDERGROUND ENVIRONMENT

by

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ABSTRACT

Tracer gas measurement is an advantageous technique for evaluating mine ventilation problems. A portable instrument capable of rapid tracer gas measurements in an actual mining environment would be a most valuable tool. This report describes a prototype instrument which was used in the uranium mines of Elliot Lake, Ontario.

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ANALYSEUR SÉQUENTIEL RAPIDE DE GAZ TRACEURS CONÇU POUR UN USAGE EN MILIEU SOUTERRAIN

par

D.J. Kennedy*

RÉSUMÉ

L'étallonnage des gaz traceurs est une technique utile lors de l'évaluation des problèmes de ventilation à l'intérieur d'une mine. Un appareil portatif capable d'étalonner rapidement les gaz traceurs dans l'environnement minier serait un outil des plus précieux. Le présent rapport contient une brève description du prototype d'un tel appareil qui a été utilisé dans les mines d'uranium à Elliot Lake en Ontario.

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INTRODUCTION

The Cape Breton Coal Research Laboratory uses SF_6 as a tracer gas to investigate mine ventilation problems. To date, this has been limited to a grab sample technique with subsequent laboratory analysis. A portable instrument capable of real-time in situ analysis of SF_6 in mine air at ppb levels would improve our capabilities and greatly extend the scope of our investigations. The instrument described in this report is a first step in that direction.

INSTRUMENT PACKAGE

The tracer gas analyzer is an automated gas chromatograph using an electron capture detector. This instrument is capable of measuring SF_6 in mine air at parts per billion (ppb) levels once every 7 seconds. The analyzer was constructed as follows:

1. COMPONENT LIST

a) One Valco 8-port gas sampling valve with matched 50 µl sample loops and helical-drive air actuator.

b) One Valco 8-port switching valve with helical-drive air actuator.

c) Four 3-way solenoids for "pulsed" operation of the above air actuators.

d) Valco digital valve sequence programmer (4 interval).

e) Two 3.2 mm x 457 mm (1/8" x 18") stainless steel columns packed with molecular sieve 5A (80/100 mesh).

f) S-Cubed electron capture detector and electrometer. The detector uses a 300 mCi Tritium source. The electrometer has a 5-position range control (A to E) corresponding to an approximate attentuation from 51.2 for E to 1024 for A.

g) Perkin-Elmer Model R100A microcomputer controlled chart recorder (100 chart units equal 230 mm for this recorder).

2. CARRIER GAS SUPPLY

A mixture of 5% methane in argon is used as the electron capture flow gas. This is delivered at constant pressure to the gas chromatograph by a Matheson Model 3102 dual-stage regulator. The in-line purification system consists of an oxygen trap (Chromatographic Specialities, Model OT3-4), a hydrocarbon trap (Applied Science, #14633) and a molecular sieve trap (Alltech Associates, S.S. hydro-purge #14515).

3. INSTRUMENT PLUMBING

Figure 1 shows a schematic of the instrument's plumbing. The carrier gas is spilt into three streams, one is passed through a restrictor, R-1, before entering a sampling valve, A. A second stream is used to alternatively backflush either column 1 or column 2. The third stream passes through another restrictor, R-2, and mixes with the effluent from valve B before entering the electron capture detector.

Valves A and B are 2-position 8-port valves. Valve A has two matched 50 µl sample loops (less than 0.2% difference in volume was measured between the matched loops). In position 1, loop L-1 is connected to the sample in/sample vent lines and loop L-2 is connected to carrier gas in (after R-1) and valve B.

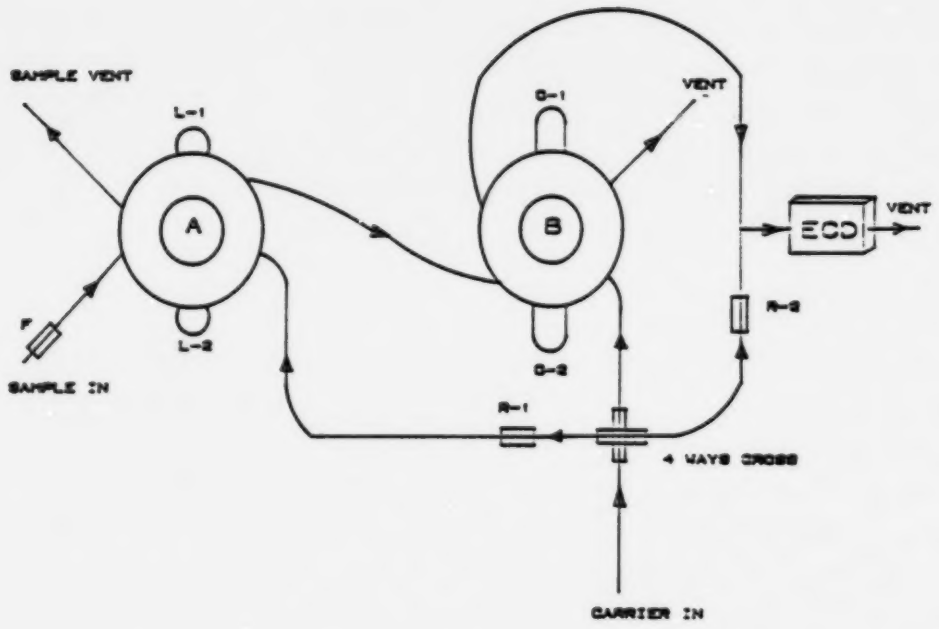
Switching valve A to position 2 connects loop L-1 to the carrier gas in and valve B lines and loop L-2 to the sample in/sample vent lines. Thus, the sample in loop L-1 is injected into the carrier gas stream on its way to valve B and loop L-2 is brought into position to receive another sample.

Valve B in position 1 connects column 1 between valve A and the electron capture detector. Column 2 is backflushed to vent by carrier gas at the same time. Switching valve B to position 2 connects column 2 between valve A and the detector and places column 1 in the backflush to vent mode.

4. RESTRICTORS

Restrictor R-1 is used to limit the carrier gas flow through the analytical column to approximately one half of the backflush rate. A MS5A column [3.2 mm x 457 mm S.S. (1/8" x 18")] is used for this purpose.

Restrictor R-2 is used to control the flow of make-up gas to the electron capture detector. A 180 mm length of 1.6 mm O.D. x 0.25 mm I.D.



A	8-port dual loop gas sampling valve
B	8-port switching valve
F	In-line filter
L-1, L-2	50 µl gas sample loops
C-1, C-2	MS5A columns, 32 mm x 457 mm (1/8" x 18") stainless steel
R-1, R-2	Flow restrictors
ECD	Electron capture detector

Figure 1 - Instrument plumbing

(1/16" x 0.01") stainless steel tubing provides this restriction. Besides replacing an expensive needle valve, this method also eliminates any contamination and/or leakage problems associated with the valve packing.

5. IN-LINE FILTER

An in-line filter is necessary to protect the gas sampling valve from dust particles. A low volume, low pressure drop filter was constructed from a 1.6 mm to 3.2 mm (1/16" to 1/8") zero volume column end fitting and a 1.6 mm to 3.2 mm (1/16" to 1/8") tube to tube stub reducer. A fine mesh screen was placed at the bottom of the column end fitting with a plug of glass wool above it. This is held in place by the tube reducer. The internal volume of the tube reducer is in the order of 130 µl. The total internal volume of the filter is less than 200 µl.

6. CLEANING PROCEDURE

The electron capture detector is extremely sensitive to electrophilic substances. This is an advantage to the analyst in the search for trace amounts of these compounds, however this sensitivity renders the detector very susceptible to contamination. To minimize contamination problems all fittings and tubing used in the gas chromatograph were subjected to the following cleaning process:

Step 1) Ultrasonic cleaning in a detergent/distilled water solution.
Step 2) Rinsing with distilled water.
Step 3) Rinsing with acetone (pesticide grade).
Step 4) Rinsing with hexane (pesticide grade).
Step 5) Drying at elevated temperature.

All lengths of tubing were heated to at least 200°C with clean carrier gas flowing through them.

7. COLUMNS

Molecular sieve 5A (80/100 mesh) is used as the column packing material. A washed molecular sieve obtained from Alltech Associates gave good results. The columns were made from 3.2 mm O.D. x 457 mm (1/8" x 18")

lengths of stainless steel tubing and zero volume column end fittings with 25 micron stainless steel sintered frits (Swagelok, #SS-200-6-1ZVSG).

It is difficult to obtain two G.C. columns with identical characteristics. Several columns were filled with molecular sieve and conditioned overnight at 350°C. Two of these with closely matched pressure drops were selected for the instrument. At a cylinder pressure of 172 kPa these gave a carrier flow rate of 18.5 and 18.2 ml/min with a retention time for SF_6 of 8.6 and 9.0 seconds respectivley.

With a concentration of 20 ppb SF_6 in air peak heights of 63 and 61 chart units on B range were obtained. Figure 2 shows the separation of SF_6 from air at a carrier flow rate of 18 ml/min. Figure 3 shows the same separation at a carrier flow rate of 33 ml/min.

8. CALIBRATION

Although the instrument is capable of an analysis every 7 seconds (Figure 4 shows instrument response from 5 to 25 ppb SF_6 in air at this sampling rate) it was decided to set the sampling rate to once every 15 seconds for our field trials. The following instrument conditions are used for the rest of this discussion:

Temperature	ambient
Analytical flow rate	18 ml/min
Backflush flow rate	36 ml/min
Make-up gas rate	78 ml/min
Valve Program Sequence on Auto	
Interval 1 (Valve A, position 1 to 2)	10 seconds
Interval 2 (Valve B, position 1 to 2)	5 seconds
Interval 3 (Valve A, position 2 to 1)	10 seconds
Interval 4 (Valve B, position 2 to 1)	5 seconds

A Matheson Model 8250 Series Dyna-Blender was used to prepare a series of calibration standards. This system mixed SF_6 free air with a standard of 72 ±2 ppb SF_6 in air at controlled flow rates directly into the gas sampling valve of the chromatograph.

Figure 5 shows the response of the instrument to concentrations of SF_6 in air from 5 to 72 ppb. The response becomes non-linear above 20 ppb.

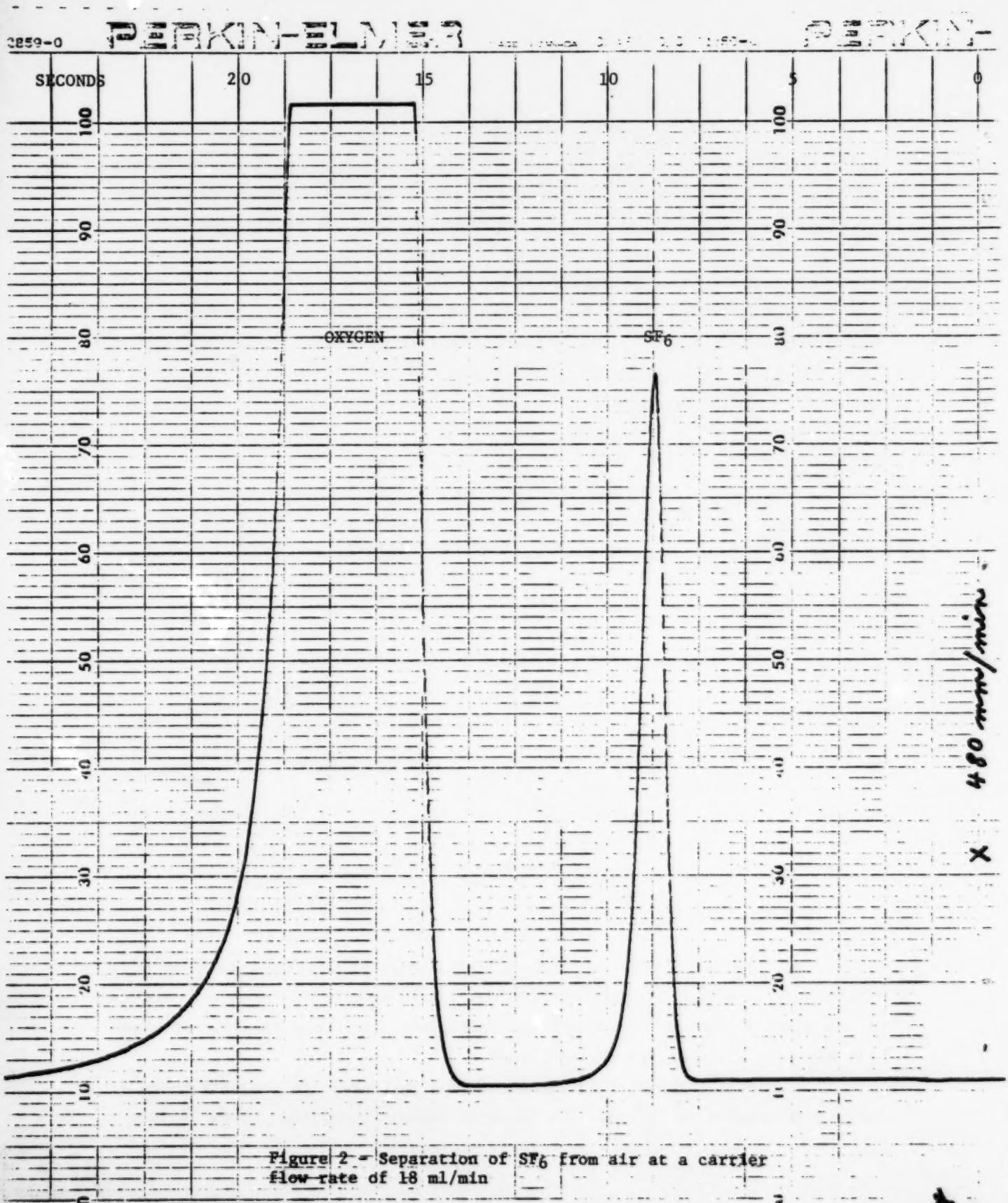


Figure 2 - Separation of SF_6 from air at a carrier flow rate of 18 ml/min

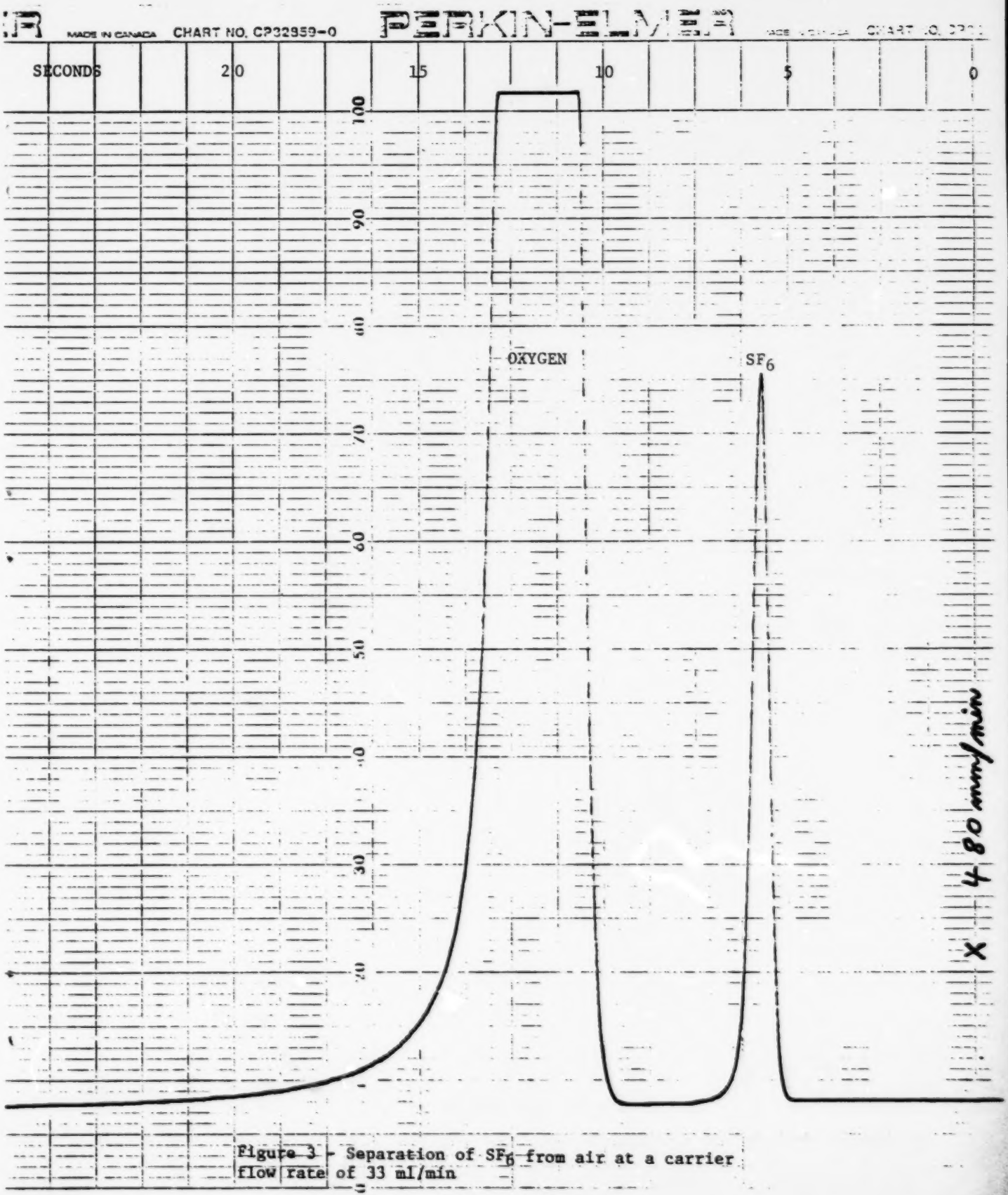


Figure 3 - Separation of SF_6 from air at a carrier flow rate of 33 ml/min

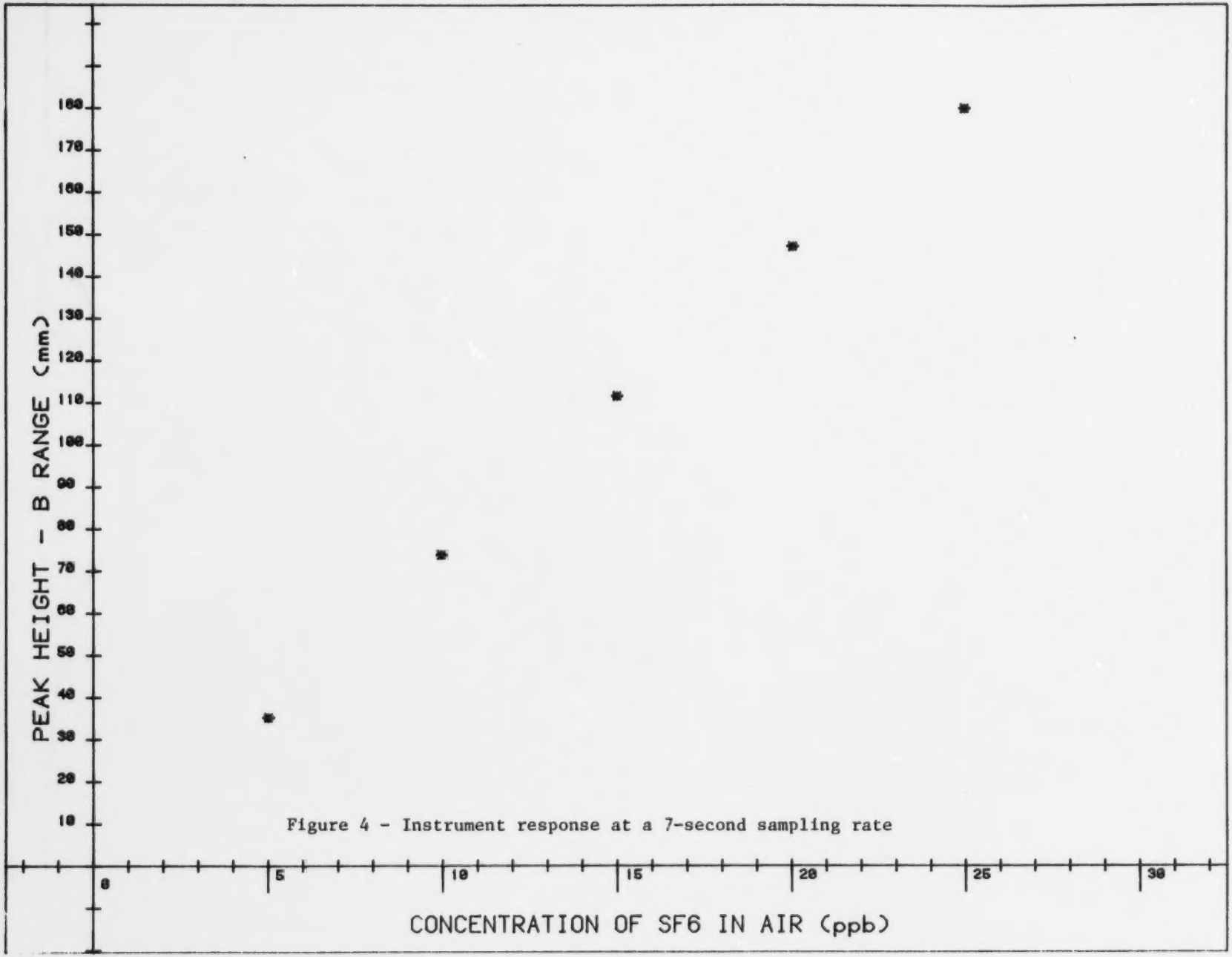


Figure 4 - Instrument response at a 7-second sampling rate

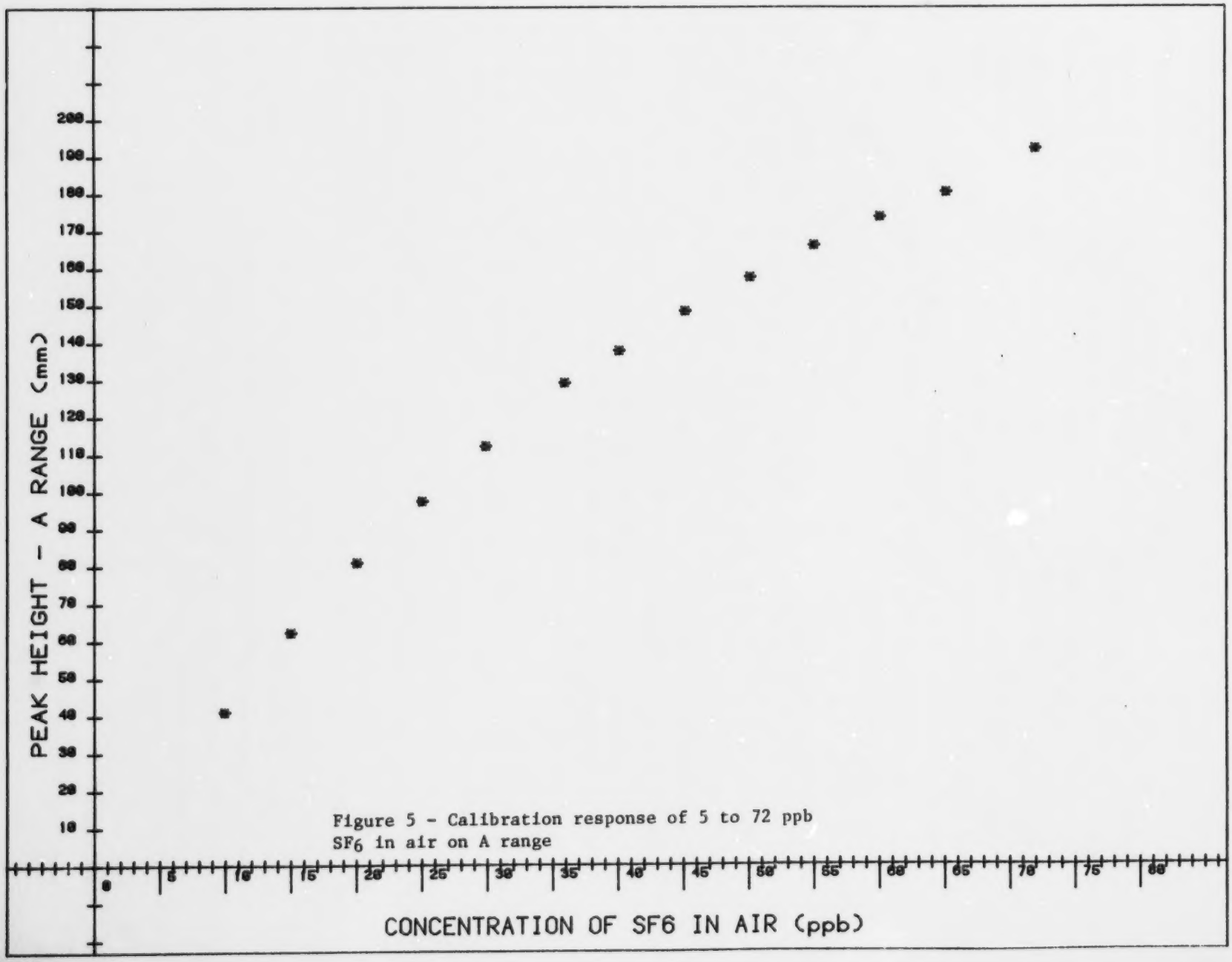


Figure 5 - Calibration response of 5 to 72 ppb SF_6 in air on A range

Figures 6 and 7 show the response from 0.5 to 20 ppb in 1 ppb steps. This elongated S-shaped curve appears typical of the SF_6 response with a MS5A column and an electron capture detector. The absolute response and the ultimate shape of the calibration curve depends on both instrument parameters and the purity of carrier gas used. To achieve an accuracy greater than 10%, the author feels it is necessary to prepare a multipoint calibration curve over the range of interest. This must be repeated before and after each field survey and with each new cylinder of carrier gas used in the instrument. In the field, single point calibration is adequate to determine absolute response.

9. SAMPLE INTRODUCTION

Standard procedure for injecting a gas sample by means of a gas sampling valve involves stopping the sample flow after the sample loop is flushed (1). Ensuring that the gas in the loop is always at atmospheric pressure before injection gives precise reproduction of sample volumes. This technique is not practicable for rapid sequential sampling.

A low pressure drop filter and 1.6 mm O.D. x 0.76 mm I.D. (1/16" x 0.03") lines are used to minimize pressurization of the sampling loops. A flow rate of 75 cc/min was chosen for the gas sampling valve. A flow rate of 50 cc/min results in a 1% increase in the SF_6 response compared to injecting the same sample at atmospheric pressure. A flow rate of 100 cc/min gives a 2% increase.

A MSA Fixt-Flo pump delivers mine air samples to the instrument. This pump has a pulsation damper which minimizes pulsations in the sample flow. A flow rate of 2 l/min is used with a portion of the pump effluent directed to the gas sampling valve. This allows rapid flushing of gas sampling lines.

A simple switching valve allows expeditious selection of either the sampling stream or a standard stream. A rotameter connected to the vent of the gas sampling valve provides an adequate indication of the flow rate through the valve.

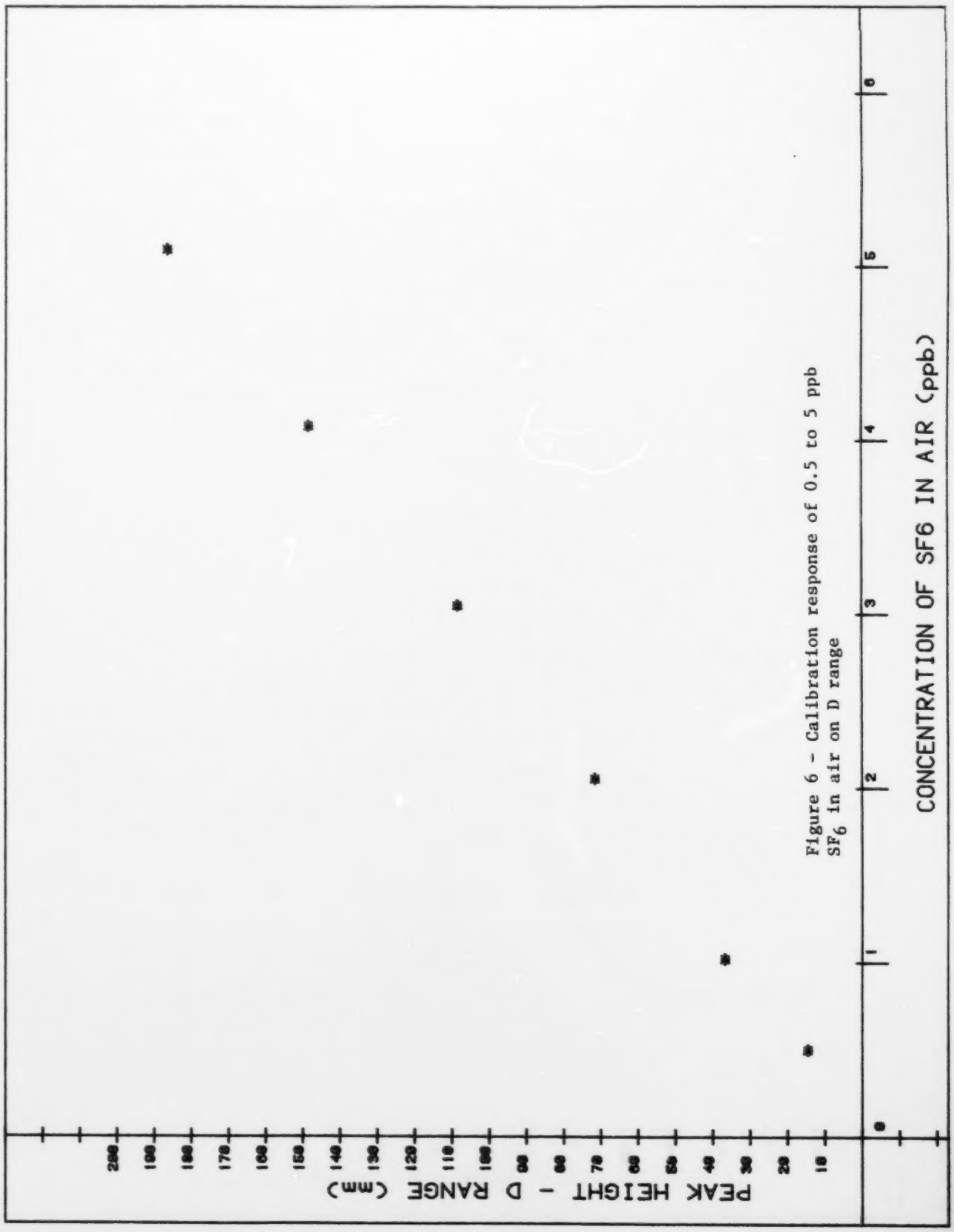


Figure 6 - Calibration response of 0.5 to 5 ppb SF_6 in air on D range

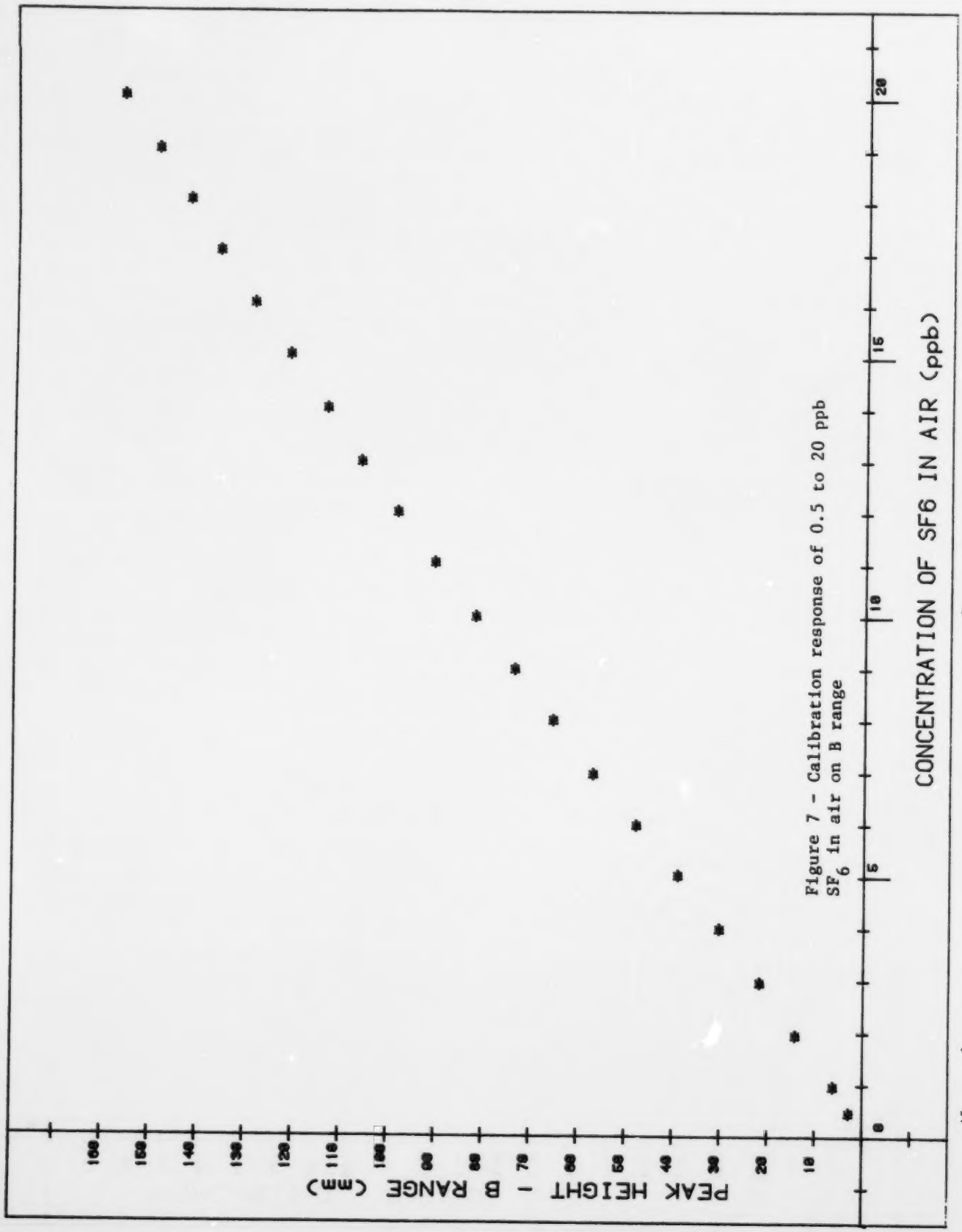


Figure 7 - Calibration response of 0.5 to 20 ppb SF_6 in air on B range

FIELD TRIALS

The underground trials took place in a uranium mine owned by Rio Algom Ltd. in Elliot Lake, Ontario. The results of these field trials are described in a separate paper (2). The instrument package was transported by road from Sydney, N.S. to Elliot Lake, Ontario a distance of 2000 km. The original intention was to have a small gas cylinder and regulator enclosed in a case with the gas chromatograph. Unfortunately, due to supply delays, we had to used a size 22 cylinder of carrier gas underground. The cylinder was 178 mm (7") in diameter by 1245 mm (49") in height and weighed 29 kg (65 lbs). This meant assembling the carrier gas system underground with the associated time delay until instrument stabilization. The following steps were taken to minimize this delay and allowed us to achieve overnight stabilization:

1) Carrier gas lines were 1.6 mm O.D. x 0.76 mm I.D. (1/16" x 0.03") stainless steel tubing.
2) The carrier gas filter system was flushed and pressurized in the laboratory.
3) The inlet to the filter system consisted of a cross-pattern shutoff valve (Whitey, Model SS-1KS4-4). This permitted thorough flushing of the regulator and gas line before carrier gas was directed to the filter. The outlet line from the filter was then flushed before it was connected to the gas chromatograph.

The environmental conditions to which the instrumentation was exposed during the field trials were typical of those found in most underground mines. Air temperature was 10°C with relative humidity fluctuating from 75% to 95%. One advantage of the underground environment was a constant temperature. Better instrument stability was achieved underground than we normally experienced in the laboratory. Over a 4½-hour period the baseline drift was a gradual increase of 1½ chart units and a standard of 14 ppb SF_6 in air varied from 47.6 to 47.8 chart units on B range.

FUTURE DEVELOPMENT

A sampling rate of once every 10 seconds is adequate for most of our field work. A disadvantage with our present method is the need to go over a large number of recorder charts in order to quantify our results. A system is needed to digitize the electron capture detector output, measure and store the SF_6 peaks and transfer this data to a computer. A computer program incorporating the instrument calibration curve could quantify field data and enable us to rapidly evaluate mine ventilation problems.

The instrument package should be housed in a single transportable case with self-contained power and gas supplies.

REFERENCES

1. Thompson, B. "Fundamentals of gas analysis by gas chromatograph"; Varian Associates Inc.; 1977.
2. Stokes, A.W. and Hardcastle, S.G. "Field trials of a rapid sequential tracer gas analyzer"; Division Report ERP/CRL 86-61(TR); CANMET, Energy, Mines and Resources Canada; 1986.